

HOW FIELD-SCALE EVIDENCE OF ABIOTIC CAH DEGRADATION PROCESSES CAN OR SHOULD IMPACT YOUR REMEDY PLANNING AND IMPLEMENTATION EFFORTS

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Introduction

The objective of this presentation is to illustrate that consideration of abiotic degradation processes during development of a site-specific conceptual site model (CSM), and ultimately the remedy performance model, may lead to a substantially different interpretation of field data and result in changes in recommendations for site-specific short- and long-term remediation strategies. Of particular interest is the use of enhanced bioremediation strategies in environments that may be dominated by abiotic degradation processes. A lack of understanding of the importance and significance of abiotic degradation processes in all groundwater systems could compromise the effectiveness of implemented engineered response actions (RAs). A brief review of a Department of Defense (DoD) case study will be provided, to demonstrate the significance of natural abiotic processes that may be controlling the release, transport, and fate of chlorinated aliphatic hydrocarbon compounds (CAH) in a groundwater plume that may not be significantly affected by biological degradation processes or conventional groundwater extraction operations. The importance of these processes in understanding the basis for CAH mass treatment and containment will be described, particularly as they are relevant to establishing remedial strategies that can be easily sustained without significant RA operations and maintenance (O&M) costs. The presentation will conclude with a summary of the additional information that may be available for most CAH sites, or can be easily collected, to support appropriate and phased implementation of treatment/containment strategies, including enhanced bioremediation techniques.

Background

The primary control on the diversity and metabolism of all plants and animals, including microorganisms, is the nature of carbon and energy sources. Consequently, before implementing an engineered remediation system designed to enhance CAH biodegradation potential, it is important to correctly characterize what processes control the nature of carbon and energy sources that may be involved in CAH degradation reactions. Microorganisms accumulate at soil particle surfaces where potential energy sources and nutrients are concentrated. Microbial populations concentrate at these surfaces because there is a greater availability of energy sources and nutrients present at the soil/water interface than within the water column itself. In fact, successful microbial growth depends on forming and sustaining structured microbial surface colonies (often called biofilms). Microbial communities attached to particle surfaces survive longer, grow faster, and degrade CAHs more quickly than those microorganisms that are not attached (i.e., those transported in the aqueous phase). Yet, the significance of processes that may dominate at the soil particle surface, and therefore control the vigor of any natural or enhanced bioremediation potential, is not typically considered during remedy planning, or engineered system design.

There are many processes that control the environmental fate of CAHs. Once released into the environment, CAHs may be subject to volatilization, leaching and other mass transport processes, adsorption/desorption and sequestration within the soil matrix, plant uptake, abiotic transformations, and biodegradation. All of these processes influence the fate of CAHs in the subsurface; all co-exist and contribute to the long-term concentration, mass, toxicity, mobility, and persistence of CAHs. To grant primacy to any one of these processes, to the exclusion of the others, ignores the complexity of processes that contribute to the fate of CAHs in the environment, and may lead to a misrepresentation of which process dominates CAH fate. Biodegradation

currently is believed to be the primary force in CAH degradation, based on extensive laboratory work on microbial metabolic activity. This emphasis has led to the proliferation of enhanced bioremediation strategies, which are designed to accentuate naturally-occurring biotic catalysts.

Yet, extrapolating laboratory results on microbial metabolic activities, which generally are developed under simple and controlled conditions, may lead to inappropriate conclusions regarding the significance and importance of microbial activity in complex, natural systems. The geochemistry of a contaminated system must be factored into the remedy planning process, to understand how the system will chemically evolve over time without intervention (i.e., engineered remediation). Too often, in a rush to effect some type of measurable change in the chemical composition of the impacted environment, we fail to recognize the natural tendency of the system. For instance, once a natural system has been disrupted by a release of CAHs, a series of reactions will be set into motion as the system moves back to equilibrium conditions. These reactions include mineral precipitation/dissolution reactions (weathering), complexation, adsorption, and oxidation/reduction reactions.

Biotic catalysts, such as bacteria, fungi, algae, enzymes, and viruses, may facilitate and/or benefit from some of these reactions. However, natural abiotic catalysts—such as oxides, hydroxides, clays, and organic matter—will dominate these reactions, just based on the sheer mass of reactants available in the subsurface (e.g., the solid aquifer matrix itself). In fact, in 1994, the US Environmental Protection Agency (USEPA) completed laboratory studies designed to investigate the ability of different ferrous iron-bearing minerals to abiotically transform carbon tetrachloride (CT) to more innocuous byproducts (e.g., carbon dioxide) in sulfidic environments, which may not be subject to significant biological activity. The results of these evaluations indicated that CT could be degraded to different transformation products at rates that could be significant on the time scale of groundwater transport, and encouraged further development of mineral-based reactive treatment systems (e.g., zero-valent iron [ZVI] permeable reactive barriers [PRBs]) that could be components of restoration activities.

In the collective effort to rapidly “undo” past environmental damage (e.g., focused on engineered treatment/containment systems with rapid kinetics such as enhanced bioremediation strategies, biotic CAH degradation paradigms), the importance of considering natural solid/solution reactions has been neglected due to the supposedly long time-frames required for these types of reactions to have measurable effects on the mass or concentration of contaminants in the subsurface. However, given the poor performance of treatment/containment systems, which are leading to large cost-to-complete (CTC) estimates (due to the need to sustain RA systems in O&M) and schedule-to-complete (STC) estimates on the order of decades to centuries, the importance of these “slower” reactions must be considered. If these processes—which can be quite significant in certain environments on the time scale of groundwater transport—are factored into remedy planning and post-implementation assessments, our recommendations on which remedial strategy will afford us the greatest degree of sustainable mass reduction and containment in the long-term could significantly change. If the CSM does not account for these sustainable abiotic processes, which could significantly influence contaminant behavior over time, observed temporal changes in the nature or concentration of contaminants may be incorrectly attributed to other mechanisms (e.g., “active” treatment, etc.). In such circumstances, evaluations of long-term remedy performance will be difficult or impossible to complete.

Mineral-based reactive *in situ* treatment systems – at their simplest – mimic conditions in particular natural systems. However, the significance of the research related to the performance of different PRB configurations has not been widely recognized in terms of how it can contribute to our understanding of the processes that occur in natural groundwater systems. Although the exact mechanism of CAH degradation effected by these “passive” engineered systems is not fully understood, available data suggest important and interesting issues that should be considered at the field scale when evaluating characterization data and requirements, and “conventional” remedy performance data. For instance, the reaction rates achieved by these engineered systems (and therefore the appropriate barrier width needed to provide adequate contact time) appears to be a function of the concentration and morphology of reactive mineral surface area, pH, and temperature. These observations have led researchers to conclude that abiotic reaction rates in these engineered systems are controlled by chemical-reaction-limited kinetics rather than mass transport to the reactive surface. These are processes that occur at the solid/solution interface, which means that information about potentially reactive minerals at CAH sites would need to be collected and evaluated to incorporate these types of chemical reactions into a complete CSM, or remedy performance model.

Additionally, the presence of certain CAH chemical intermediates has been interpreted as *de facto* evidence of biologically mediated reductive dechlorination reactions. In fact, as elucidated by research on the performance of PRB systems, the abiotic reduction of CAH also may yield chlorinated degradation products as a result of

sequential hydrogenolysis and reductive β -elimination at the solid/solution interface. Acetylene gas—which is characteristic of an abiotic dichloroelimination reaction—can be slowly converted to ethene. Thus, the mere presence of ethene in the subsurface tells us little about the primary CAH degradation processes. Similarly, the production of hydrogen gas occurs naturally within the subsurface as a result of mineral weathering reactions. Consequently, increased concentrations of hydrogen gas near CAH release sites may be evidence of expedited abiotic weathering reactions, often accompanied by significant geochemical changes in the surrounding groundwater as minerals are released.

The role of microbial activity in these reactions may be indirect; it is possible that microbial populations are contributing to abiotic degradation processes in certain environments by producing organic ligands that act as effective mineral chelators, which hasten the abiotic weathering process (i.e., facilitated dissolution). Of course microbial populations may thrive in areas undergoing abiotic CAH degradation processes, because they may be metabolizing the organic carbon component of the aquifer matrix that is being made bioavailable by the expedited weathering processes and/or facilitating the rates at which the mineral dissolution and/or oxidation/reduction reactions occur. As noted previously, microbial catalysts are a subset of the catalysts that are operant in the environment. The importance of the biotic catalysts must be considered in the context of the inorganic catalysts. Certain inorganic components—notably clay minerals and mineral-containing oxides—may serve as significant facilitators of CAH degradation reactions. The relative significance of the abiotic reactions may actually increase at a CAH site over time as the contaminant becomes less bioavailable due to sequestration reactions that occur at the soil particle surfaces. As a CAH source ages, abiotic degradation reactions may dominate due to substrate accessibility limitations. This means that contaminant age should be accounted for in the remedial planning process. Remedial strategies should be phased over space and time to account for diminishing bioavailable contaminant mass.

Case Study

Historical monitoring data for several CAH plumes at a Defense Logistics Agency (DLA) facility, the Defense Supply Center Richmond (DSCR), suggest substantial reductions in the nature, mass, and concentration of CAH have occurred through time, including a gradual conversion from highly-chlorinated compounds (e.g., tetrachloroethene [PCE]) to less-chlorinated compounds (e.g., *cis*-1,2-dichloroethene [DCE]). Such water-quality data are often cited as one of the strongest “lines of evidence” of biotic CAH degradation processes. However, upon a closer inspection of available data, geochemical conditions in the subsurface at DSCR are not strictly consistent with biological activity. For instance, one CAH source area near an abandoned “industrial construction and debris” landfill is believed to have reduced pH in groundwater to levels that are adverse to biological activity (i.e. pH around 3). Additionally, although there is believed to be little organic carbon available to support biotic reactions, extremely high concentrations of ‘dissolved’ (labile) concentrations of redox-sensitive minerals have been measured in groundwater. Finally, the groundwater at DSCR is sporadically characterized by elevated concentrations of sulfate that should effectively limit biotic CAH degradation. Consequently, field scale data on the behavior of CAH in groundwater through time could not be credibly explained by a CSM limited to biotic degradation processes alone.

We have theorized that the geology of the water-bearing units underlying DSCR may provide mineral phases suitable for promoting and sustaining some level of abiotic CAH degradation. The aquifer matrix includes an iron-rich hornblende, which weathers to produce chlorite. Weathering reactions are typically slow, although these processes can be facilitated by concurrent redox reactions or the presence of complex organics that act as chelators (e.g., CAH, microbial enzymes). Chlorite weathers further to produce other iron-bearing minerals, ferrihydroxides, and dissolved (reduced) species (e.g., Fe^{2+}). This geochemical weathering model is confirmed by the mineralogy of the different water-bearing strata at the site. We believe that a CAH source itself – usually released and present as either residual or mobile DNAPL – may expedite the dissolution of the solid aquifer matrix, thereby mobilizing minerals and exposing additional “fresh” mineral surface area that may be available to participate in abiotic CAH degradation processes. Consequently, the very occurrence of reduced mineral species in the bulk water column may not be the result of biological activity at CAH sites; the occurrence of these minerals in the bulk water column may be the result of CAH DNAPL co-solvency effects and abiotic dissolution and oxidation/reduction reactions.

Additionally, as typical of most CAH sites, the anaerobic groundwater is characterized by significant concentrations of “dissolved” mineral phases. These labile chemical forms may be generated by CAH co-solvency effects at DNAPL sources and be supported by the formation of mineral colloid and/or complex phases. These labile forms of iron-bearing minerals may contribute to the abiotic degradation potential within the water

column itself, provided that the required electron transfer reactions can occur at mineral surfaces. At DSCR, as at many CAH sites, CAH transformation reactions observed at the field scale appear to mirror the performance of ZVI PRB systems, with rapid transformation of PCE and trichloroethene (TCE) at the source areas and slower transformation of *cis*-1,2-DCE and vinyl chloride in downgradient areas. The spatial distribution of CAH in groundwater appears markedly similar to field data reported for ZVI PRB systems, particularly with regard to the apparent decrease in reaction rates for *cis*-1,2-DCE (despite appropriate geochemical conditions) and the “geochemical shadow” of CAH degradation processes which continues downgradient from the engineered treatment zone. The former could result from abiotic chemical reaction kinetic limitations, and the latter could result from decreases in the concentration of reactive minerals that are available to support abiotic degradation reactions (i.e., reaction becomes mass transport-limited in these areas).

This type of information should be considered during the remedy planning and implementation process, to ensure that field conditions are suitable for enhancing a subset of the catalysts involved in CAH degradation. In many cases, the mineralogical characteristics alone may control CAH degradation processes, which means that engineered intervention must honor the natural abiotic tendencies of the system. Now armed with an understanding of the potential significance of abiotic degradation processes, Air Force RPMs should consider the following questions when designing an enhanced bioremediation system:

1. Does adding any energy source change the characteristics of soil particle surfaces and surrounding water quality that control microbial communities and abiotic transformations?
2. Does enhanced biological activity change soil particle surfaces to slow or terminate other CAH transformation processes?
3. Has the known effect of source ageing (i.e., diminishing contaminant bioavailability) been factored into the engineered design and performance monitoring program?
4. Has the importance of different processes that control CAHs as a function of depth been considered in the remedial design?

Therefore, we recommend that the CSM paradigm used to justify the application of enhanced CAH biodegradation systems be expanded to account for abiotic reactions commonly considered during the design of engineered PRB/RZF systems. Some of the site characterization data required to support a technically defensible geochemical model inclusive of solid and labile mineral phases may be already available, although “specialized” characterization data could be collected as part of remedial design or contingency planning phase to strengthen the technical basis of remedy plans. These data will contribute to the overall geochemical model, but do not need to be completed at every sample location. Care must be taken to balance the cost of the field effort with the risk associated with data uncertainty.